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Wetting Behavior and Evolution of Microstructure of Sn–3.5Ag Solder Alloy on Electroplated 304 Stainless Steel Substrates

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Abstract In the present study, wetting characteristics and evolution of microstructure of Sn–3.5Ag solder on Ag/Ni and Ni electroplated 304 stainless steel (304SS) substrates have been investigated. Solder alloy spread on Ag/Ni plated 304SS substrates exhibited better wetting as compared to Ni/304SS substrate. The formations of irregular shaped and coarser IMCs were found at the interface of solder/Ni/304SS substrate region whereas, solder/Ag/Ni/substrate interface showed continuous scallop and needle shaped IMCs. The precipitation of Ag_3Sn, Ni–Sn, $FeSn_2$ and lesser percentage of Fe–Cr–Sn IMCs were found at the interface of solder/Ag/Ni/substrate region whereas, solder/Ni/304 SS substrate exhibited predominantly $FeSn_2$ and Fe–Cr–Sn IMCs. Presence of higher amount of Fe–Cr–Sn IMCs at the solder/Ni/304SS substrate interface inhibited the further wetting of solder alloy.

Keywords Lead free solder · Reactive wetting · Stainless steel · IMCs

1 Introduction

Eutectic Sn–37Pb solder has been used extensively in electronic applications, because they possess advantages like low melting temperatures, better ductility and excellent wetting characteristics [1]. However, Pb (lead) is a toxic element and its toxicity towards humans and wild life has warranted the elimination of Pb from solders [2]. Most of the countries have banned the use of Pb from electronic solders for sustaining green environment. Thus, the development of new lead free solders is in rapid progress for the past ten years worldwide to replace Sn–37Pb solder. Among the novel lead free solders (Sn–Cu, Sn–Ag, Sn–Zn–Bi, Sn–Ag–Bi and Sn–Ag–Cu) invented so far, eutectic Sn–3.5Ag solder is widely used in soldering applications due to its higher ductility and thermal resistance comparable to Sn–Pb solder alloy [2, 3].

Common solderable metals such as copper, gold, nickel and silver are popularly used in the electronic industry because of their better compatibility with solder alloys. Soldering is often used for joining stainless steel in applications such as roofing and water tubing (plumbing) [4]. In industrial applications, the demand for joints of Cu/stainless steel has increased due to the advantages obtained from the properties of the bimetal because, this combination of joints is expected to prove highly beneficial in many applications ranging from automobile, rail and aviation industries to smaller, more commonly used products, such as saucepans [5]. Soldering stainless steel is difficult because, a thin tenacious self-repairing protective coating of chromium oxide film will protect its surface but inhibit liquid wetting on it [6]. Linkun et al. [7] investigated wetting behavior of Sn–3.0Ag–0.5Cu solder on 304 stainless steel substrates and concluded that solder alloy is non-wettable to stainless steel substrates in the temperature range from 230 to 400 °C. Thus, chromium oxide has to be removed before satisfactory results can be achieved. Stainless steel can be joined, if correct techniques are employed. Indium Corporation suggested Sn–3.5Ag and Au–20Sn solders for joining stainless steel [8]. An extensive study on reactive wetting of stainless

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steel substrates by solder alloy has not yet been carried out. In the present study, wetting characteristics and evolution of microstructure of Sn–3.5Ag solder on silver (Ag)/Ni and Ni electroplated 304 stainless steel (304SS) substrate is investigated.

2 Materials and Methods

To investigate the wetting behavior of solder, commercially procured Sn–3.5Ag lead-free solder (Alfa Aesar, USA) was selected as the solder material and 304 grade stainless steel substrates (304SS) electroplated with Ag/Ni and Ni were used as substrate materials. The electroplating of stainless steel was carried out at Ganesh Electroplaters, Mangalore. The average surface roughness (R_a) of two trials for a single sample of the coated test samples were in the range of 0.01–0.016 µm. The surface roughness of coated substrates was measured using a Form Talysurf 50 surface profiler prior to the spreading experiment. Contact angle measurements were carried out using an FTA 200 dynamic contact angle analyser. Wetting experiments were conducted, by placing a solder ball (weighing approximately 0.08 g) on the surface of the electroplated cylindrical 304SS substrate (Ø12.5 × 8 mm). This pair of solder/substrate system was kept in the heating chamber after employing two to three drops of an inorganic acid flux (Alfa Aesar, USA standard flux) on the solder/base metal arrangement. The chamber was heated with the aid of an external electrical source to a temperature of about 253 °C. This temperature was maintained during the entire spreading process. Images were captured after commencement of spreading. The spreading process was recorded for approximately 32 min. The captured images were analyzed using FTA Video 2.0 software to determine the wetting behavior. The solder drop bonded to the substrate was sectioned along the axis using Isomet low speed saw (Buehler 465-ISE-00517) and polished using SiC papers of different grit sizes. The final polishing was carried out on Rotopol-21 Multidoser polishing equipment with the aid of 3, 6 and 9 µm diamond slurry and an OPS solution with their corresponding polishing pads. The solder/substrate interfacial region was micro-examined using OLYMPUS DP71 optical microscope as well as ZEISS SUPRA 55 VP scanning electron microscopy (SEM).

3 Results and Discussion

The typical relaxation curves for spreading of Sn–3.5Ag solder on electroplated 304SS substrates are shown in Fig. 1. Solder alloy spread on substrates exhibited decrease in contact angle sharply at the initial stages, and it became gradual as the solidifying solder approached equilibrium stage. Equilibrium contact angle values obtained after the spreading experiments on electroplated 304SS substrates are given in Table 1. Solder alloy spread on Ag/Ni coated 304SS substrates exhibited better wetting as compared to solder spread on Ni plated 304SS substrate. Both surface roughness and metal plating on substrates influence the wetting of solder alloy. However, in the present study, the surface roughnesses of the substrates measured were found to be almost similar. Hence, the enhancement in wettability of solder alloy on sandwich metal-coated substrate is due to the reactive wetting of solder alloy with metal plated substrate. Figure 2 shows the optical microstructures of interfaces of solder solidified on electroplated 304SS substrates and reveal that, solder/Ag/Ni/304SS exhibited continuous scallop and needle shaped IMCs at the interface whereas, IMCs formed at the interface of solder/Ni/304SS were found to be irregular in shape and coarser. It clearly shows that, in addition to the dissolution of the electroplated metal layer, the substrate metal has also undergone reaction with the molten solder in both cases.

Coarser IMCs formed at the solder/Ni/304 SS substrate interface indicates that, molten solder has dissolved Ni atoms from coated layer and exposed the base metal because, only Ni electroplating was done on 304SS substrate. Once the liquid solder dissolved Ni atoms from the

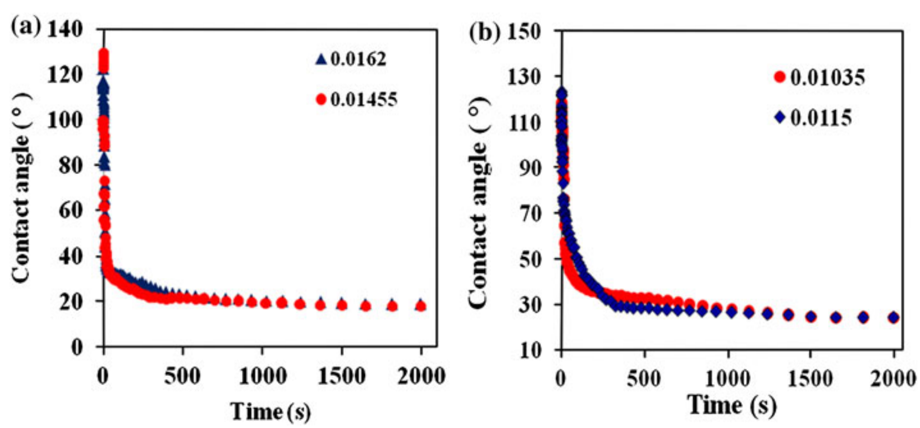

Fig. 1 Relaxation behaviours of Sn–3.5Ag solder on **a** Ag/Ni plated 304SS substrate and **b** Ni plated 304SS substrate

Table 1 Equilibrium contact angles obtained after spreading experiments for Sn–3.5Ag solder on electroplated stainless steel substrates

Electroplated 304SS substrates	Average roughness (R_a, μm)	Equilibrium contact angle (θ)
Ag/Ni/SS substrate	0.0162	18.68
	0.01455	18.73
Ni/SS substrate	0.01035	24.18
	0.0115	24.82

coated metal, the reaction products developed at the interface during spreading of molten solder, moved away from the interface into the bulk solder, due to which coarser and irregular shaped IMCs formed at the interface (Fig. 2b). However, in other case it was sandwich like coating of Ag/Ni electroplated on 304SS substrate. Thus, the Ag coating was first exposed to molten solder followed by Ni and base metal. Due to sandwich coating, most of molten solder atoms did not find the path to diffuse into the base metal initially. After the precipitation of scallop IMCs, higher activated solder atoms diffused into the base metal through the narrow gaps present between scallop and needle shape IMCs at few locations only.

Figures 3 and 4 show the SEM images with line scan analysis across solder/Ag/Ni/304SS and solder/Ni/304SS interfaces respectively. Line scan profile gives clear indication of elemental distribution in solder/substrate system. The concentration profiles shown in Figs. 3b and 4b, confirm that, concentration of Sn atoms decreases in the substrate while, concentration of Fe atoms decreases with distance away from the interface. A step like profiles of Sn and Ni atoms as shown in Fig. 3b indicates the evolution of IMC predominately of Sn–Ni in the bulk of solder alloy, which is about 1.2 μm distance from the interface. The corresponding phase is marked as A in Fig. 3a with small amount of Ag and Cu present across the interface. Cu

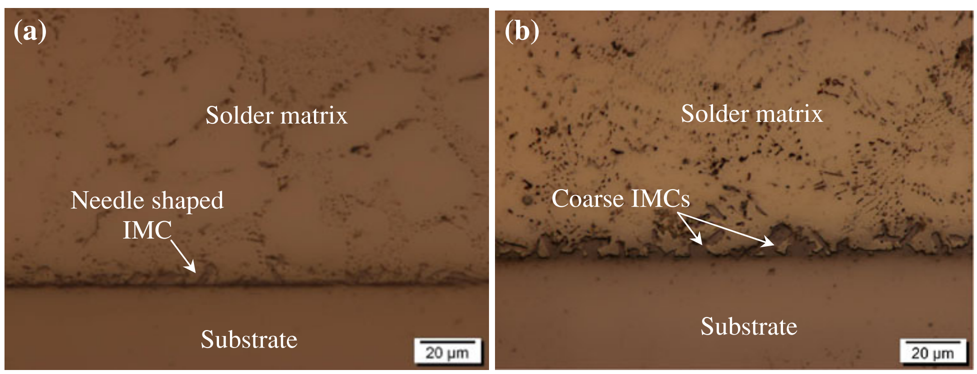

Fig. 2 Interfacial Microstructures of solder alloy solidified on **a** Ag/Ni plated 304SS substrate and **b** Ni plated 304SS substrate

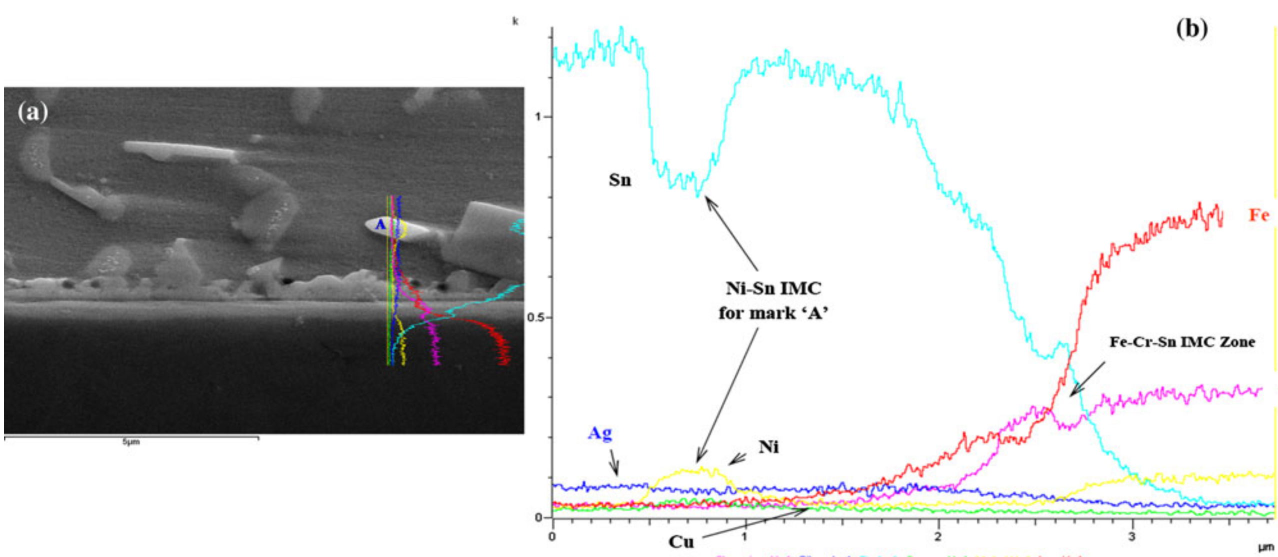

Fig. 3 **a** SEM image of solder/Ag/Ni/304SS substrate interface **b** line scan profile across solder/substrate interface

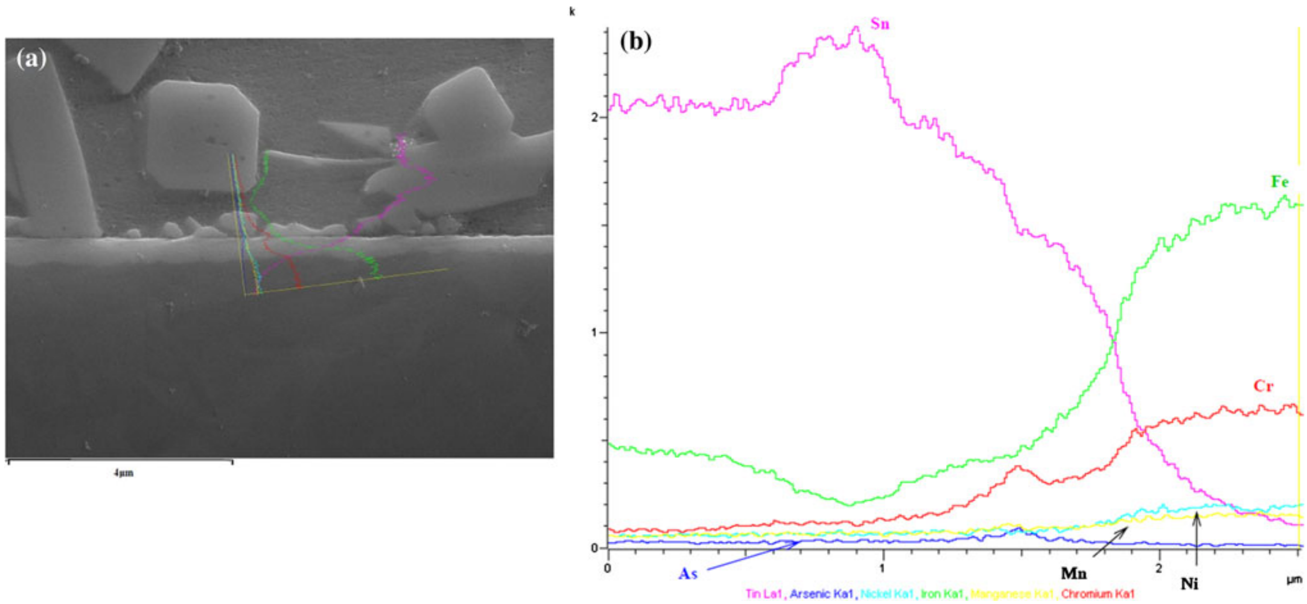

Fig. 4 **a** SEM image of solder/Ni/304SS substrate interface **b** line scan profile across solder/substrate interface

might have been introduced as an impurity during the coating process. Elemental analysis carried out at the different locations of solder/Ag/Ni plated 304SS substrate systems confirmed the presence of Ni–Sn (in the bulk), Ag_3Sn (in bulk and interface) and $FeSn_2$ IMCs at the interface. At some locations, small concentrations of precipitations of Fe–Cr–Sn IMCs were observed because, due to long period of soldering time more activated Sn atoms diffused through the narrow gaps present between scallop and needle shape IMCs. Thus, interface exhibited Fe-Sn and Fe–Cr–Sn IMCs at some locations.

Figure 4a confirms the presence of coarser and irregular shape of IMCs at solder/Ni/304SS substrate interface. In this case also, elemental analysis was carried at different locations to identify the IMCs and it was found that more precipitation of $FeSn_2$ and Fe–Cr–Sn IMCs found at the interface as compared to solder/Ag/Ni/304SS substrate interface region. Since, the concentration of Cr atoms in base metal is higher as compared to other alloying elements, hence Fe–Cr–Sn IMCs found at the interface. Another reason is that, after dissolution of Ni layer in molten solder, base metal was directly exposed to liquid solder. In most cases the elemental composition of Fe–Cr–Sn IMCs found to be in the proposition of $(Fe,Cr)Sn_2$. Tadashi and Masaharu [9] also reported the presence of these IMCs at the interface of solder/304SS substrate. It clearly indicates that formation of higher amount of Fe–Cr–Sn IMCs at the solder/Ni/304SS substrate interface inhibited further wetting of solder alloy. Consequently, it is possible to solder 304 stainless steels at temperature 253 °C if appropriate sandwich like surface coatings are done.

4 Conclusions

In the present study, wetting behavior and evolution of microstructure of Sn–3.5Ag solder on electroplated 304 stainless steel substrates was investigated. The solder alloy exhibited better wetting ($\theta = 18.73°$) on Ag/Ni coated 304SS substrates as compared to that on Ni plated 304SS substrates ($\theta = 24.5°$). Solder/Ag/Ni/304SS interface exhibited continuous scallop and needle shaped IMCs at the interface whereas, solder/Ni/304SS interface IMCs were found to be irregular and coarser. Solder//Ni/304SS substrate interface exhibited more precipitation of $FeSn_2$ and Fe–Cr–Sn. The presence of higher amount of Fe–Cr–Sn IMCs at the solder/Ni/304SS substrate interface inhibited further wetting of solder alloy resulting in higher contact angle.

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